

CeO₂ and TiO₂ obtained by urea assisted homogeneous hydrolyses method as catalysts for environmental protection: Effect of Ti/Ce ratio

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In present study mesoporous titanium–cerium oxide materials with different composition were prepared by homogeneous precipitation with urea. The samples were characterized by nitrogen physisorption, XRD, UV–Vis, Raman, temperature programmed reduction and their catalytic properties were studied in methanol decomposition and oxidation of ethyl acetate. The effect of phase composition on the texture, structure and redox properties was discussed in close relation with their catalytic activity. It was found that the catalytic behavior of the samples in the methanol decomposition and ethyl acetate oxidation, could be successfully controlled by the Ti/Ce ratio.

Keywords: nanostructured oxides, ethyl acetate combustion, methanol decomposition.

INTRODUCTION

Recently, titanium oxide has received much attention in technological areas due to its superior electrical, optical, and photo-catalytic properties [1, 2]. The application of titania as catalyst or catalyst support is strongly related to its crystal structure, surface density of hydroxyl groups, specific surface area, porosity, particle size, etc. [2, 3]. A lot of data in the literature have demonstrated that catalytic activity of TiO₂ materials could be increased by the introduction of various additives due to improved dispersion and redox properties of the mixed nanocomposites. Among them, the titania-ceria binary oxides have been intensively studied in various reactions, such as total oxidation, steam reforming, decomposition of nitrogen oxides, etc [4]. Monteros et al. [5] show that the isomorphic substitution of Ce ions into TiO₂ lattice generates oxygen vacancies, which stabilizes the anatase phase, increases the specific surface area and the dispersion of the metal oxide particles. Dutta et al. [6] demonstrated enhanced reducibility of ceria–titania solutions. Yang et al. [7] reported higher catalytic activity of ceria–titania catalysts than the pure oxides in aqueous-phase oxidations. It has been also demonstrated that

the homogeneous co-precipitation method favors the deposition of finely dispersed CeO₂ on TiO₂, which makes it highly active in selective oxidation of nitrogen oxides. The aim of current investigation is to obtain series of Ti-Ce composites with different composition by urea assisted homogeneous hydrolyses method. The obtained materials were characterized by nitrogen physisorption, XRD, UV–Vis, Raman- spectroscopies and TPR. The relation between the phase composition, structure, texture and surface properties of the obtained materials and their catalytic behaviour in methanol decomposition as a source of syngas and total oxidation of ethyl acetate as a representative VOCs was discussed.

EXPERIMENTAL

The ceria-titania samples were synthesized by urea assisted homogeneous hydrolyses method as was described in [8]. The samples were denoted as Ti_xCe_y, where x:y was the metal mol ratio, which in bi-component samples was 2:8, 5:5 or 8:2. The textural characteristics were collected from nitrogen adsorption-desorption isotherms measured at 77 K using a Quantachrome NOVA 1200 apparatus. Powder X-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer with Cu K α radiation using a LynxEye detector. The UV–Vis spectra were recorded on a Jasco V-650 UV-Vis spectrophotometer equipped with a diffuse

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reflectance unit. Raman spectra were acquired with a DXR Raman microscope using a 780 nm laser. The TPR/TG analyses were performed on a Setaram TG92 instrument using a flow of 50 vol.% H₂ in Ar. The catalytic oxidation of ethyl acetate was performed in a flow type reactor (0.030 g of catalyst) with a mixture of ethyl acetate in air (1.21 mol %) and WHSV of 100 h⁻¹. Methanol conversion was carried out in a fixed bed flow reactor (0.055 g of catalyst), argon being used as a carrier gas and methanol partial pressure of 1.57 kPa. On-line gas chromatographic analyses were performed for both reactions using an absolute calibration method and carbon based material balance.

RESULTS AND DISCUSSION

Textural characterization of the obtained materials was carried out by low temperature nitrogen physisorption (Fig. 1a, Table 1). All samples exhibited type IV isotherms with a sharp inflection of adsorbed nitrogen volume at a relative pressure (P/P_0) of about 0.8 (type H2 hysteresis loop), indicating the existence of mesopores. The shape of the hys-

teresis loop changed with the samples composition indicating domination of cage-like pores for TiO₂ and all bi-component Ti-Ce and slit-like pores for CeO₂. The addition of cerium to TiO₂ leads to an increase in the surface area, pore volume and average pore volume and this effect is most pronounced for 8Ti2Ce sample (Table 1). The observed improved textural parameters significantly overcame the expected ones if the samples were considered as a mechanical mixture of the individual oxides.

The XRD patterns of the prepared mesoporous Ti-Ce oxides are shown in Figure 1b. Diffraction peaks typical of highly crystalline TiO₂ with average crystallite size of about 13 nm and anatase structure are observed for the mono-component titania [1] (Fig. 1b). The XRD pattern of ceria consists of reflections typical of face centered cubic fluorite phase with average crystallite size about 13 nm [4]. Anatase phase was only registered when titania was doped with small amount of ceria (8Ti2Ce), but the reflections were broader as compared to pure TiO₂, which evidences higher dispersion of TiO₂. For the samples with higher ceria content, the characteristic of ceria reflections were only registered. The observed slight decrease of unit cell parameters for the

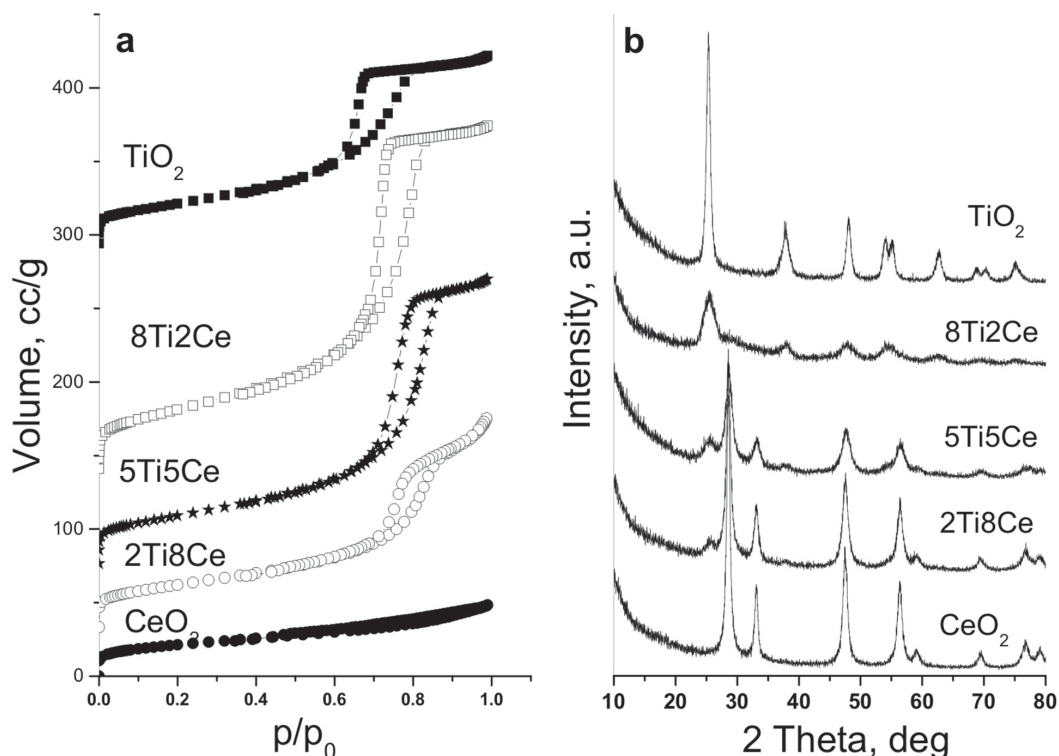


Fig. 1. Nitrogen physisorption isotherms (a) and XRD patterns (b) of TiCe materials. (The curves are shifted in y direction for better comparison).

Table 1. Nitrogen physisorption data of mono- and bi-component TiCe materials

Sample	BET m ² g ⁻¹	Vt cm ³ g ⁻¹	Average pore diameter, nm	SA, EA mol.m ⁻²	SA, MD mol.m ⁻²
TiO ₂	97	0.19	5.91	0.23	0.54
8Ti2Ce	146	0.36	7.98	0.31	0.36
5Ti5Ce	117	0.30	9.05	0.65	0.53
2Ti8Ce	107	0.21	3.23	0.78	0.60
CeO ₂	76	0.07	3.80	1.09	0.60

*BET-surface areas; Vt – pore volume; *SA – specific catalytic activity (600K)

ceria component in binary materials as compared to the individual CeO₂ sample does not exclude substitution of Ce⁴⁺ ion by smaller Ti⁴⁺ ion [5].

Diffuse reflectance UV–Vis spectra of all Ti–Ce materials were presented in Figure 2a. The spectrum of CeO₂ represents a well visible absorption band in the 300–500 nm range, which is typical of pure ceria phase. The absorption at 355 nm in the TiO₂ spectrum is related to presence of anatase phase. It is clearly seen, that ceria doping of titania results in shift of the adsorption edge to the visible region which is slightly influenced by the Ti/Ce ratio. In accordance with the XRD and nitrogen physisorption data, the increasing absorption feature for all mixed materials could be assigned to changes in the environment of both metal ions due to the better dispersion of metal oxides and/or to the appearance of strong interaction between them. The

structural changes in the bi-component materials as compared to the individual oxides are well illustrated by Raman spectra (Fig. 2b). Raman spectrum of pure TiO₂ represent bands at about 141, 198, 398, 515 and 644 cm⁻¹ typical of anatase phase [7]. The observed slight blue shift of the main mode to 151 cm⁻¹ could be an indication for the changes in the environment of titanium ions in anatase lattice. The decrease in the intensity of this peak accompanied with its slight broadening for all bi-component samples could be due to particle size decrease, which is in accordance with the XRD data. The strong peak at 460 cm⁻¹ in the spectrum of CeO₂ is attributed to its fluorite type structure [4]. In the mixed oxides spectra the intensity of the main peak of ceria significantly decreased. In accordance with the XRD and UV-Vis data this could be assigned to the improved metal oxide dispersion and formation of

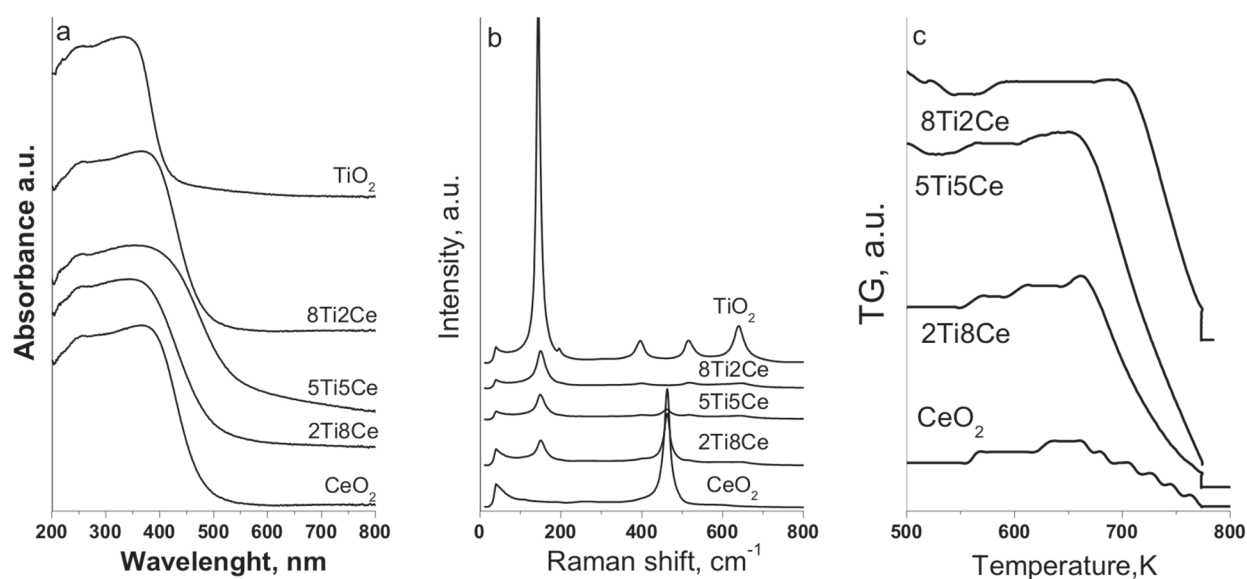


Fig. 2. UV-Vis spectra (a), Raman spectra (b) and TPR-TG profiles (c) of TiCe materials.

mixed oxide phases, due to the incorporation of Ti⁴⁺ ions into the ceria lattice. In order to study the nature of the obtained metal oxide species in detail, TPR measurements were carried out. In case of pure ceria (Fig. 2c), the reduction was initiated just above 657 K. Here, the observed weight loss up to 773 K corresponded to about 4% reduction of Ce⁴⁺ to Ce³⁺ ions. The reduction effect for bi-component material with high ceria content (2Ti8Ce) was significantly shifted to lower temperature, which was combined with an increase in the reduction degree (about 10%). The increase in titania content (5Ti5Ce) led to the increase of the reduction ability, which was clearly demonstrated both with the shift of the reduction profile to lower temperature as well as by the increase in the overall reduction degree (up to 13%).

However the reduction of 8Ti2Ce material significantly decreases (8%), despite it is still easier as compared to pure CeO₂. Thus, TPR results clearly demonstrate the existence of interaction between different metal oxide species in bi-component materials, which results in the presence of more readily reducible and finely dispersed metal oxide crystallites interacted with titania. In accordance with the XRD and Raman analyses, the improved reducibility of the mixed oxides could be due to the incor-

poration of Ti⁴⁺ ions into the ceria lattice, but this effect strongly depends on the Ti/Ce ratio.

The temperature dependencies of catalytic activity for all mono- and bi-component materials in total oxidation of ethyl acetate are presented in Figure 3a. Beside CO₂ which is the most important product of EA oxidation, ethanol (EtOH), acetaldehyde (AA) and acetic acid (AcAc) are also registered as by-products (Figure 3b). Among all materials, pure mono-component ceria compound exhibit the highest catalytic activity, but low selectivity to CO₂ due to the formation of ethanol as byproduct. The pure titania sample demonstrated significantly low catalytic activity combined with high ability to formation of by-products, mainly AA, EtOH and ethane. All bi-component materials exhibit higher catalytic activity than pure TiO₂ and this tendency increases with the increase of Ce content in them. However their activity was less than the observed one for pure CeO₂ sample. With the exception of 2Ti8Ce, the selectivity to CO₂ formation for the binary materials remained relatively low (about 50% at 50% conversion) and very close to that one of the individual oxides. In order to elucidate the effect of different specific surface area of the samples on their catalytic behaviour (Table 1), the specific catalytic activity was calculated as conversion at selected

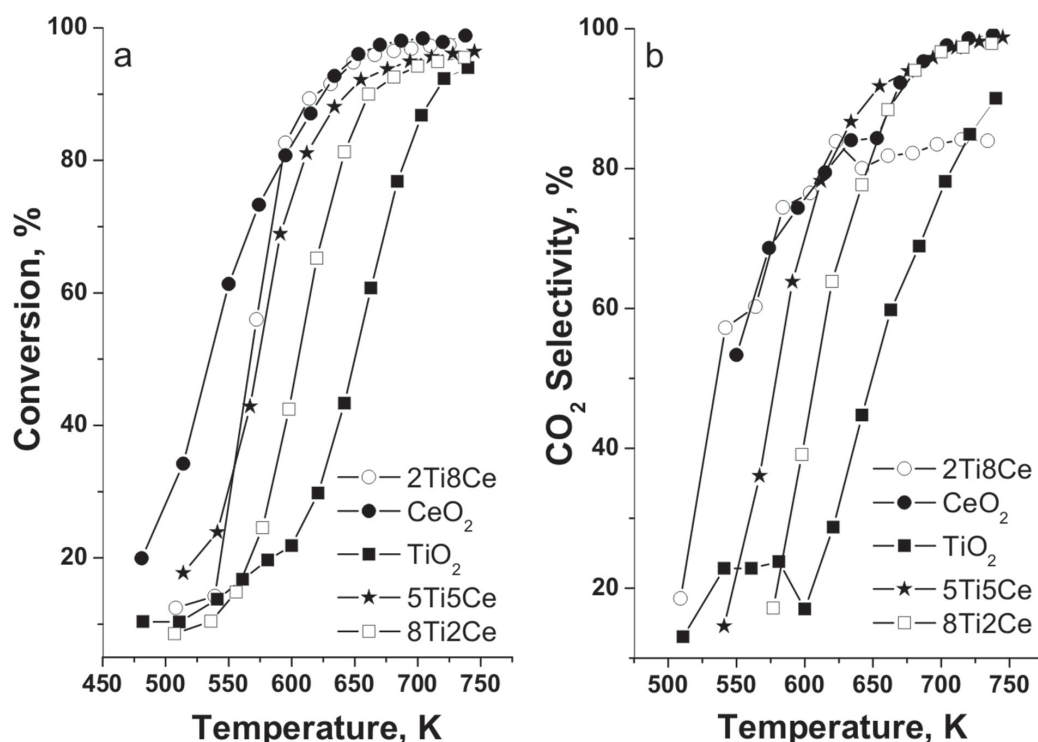


Fig. 3. Ethyl acetate conversion (a) and selectivity to CO₂ (b) of TiCe materials.

temperature (600 K) per unit surface area. The obtained results demonstrate well defined tendency of its increase with ceria content in the bi-component samples and the highest value is observed for pure CeO₂. However, the deviation from the linear dependency of the specific catalytic activity vs Ce content urge the authors to assume that the improvement of the catalytic activity in binary materials is not simply related to their higher surface area as a result of the improved dispersion. We can not fully exclude the contribution of the improved mobility of lattice oxygen in ceria due to the incorporation of Ti⁴⁺ ions in it, which was well illustrated by the TPR measurements (Fig. 2c). This promotes ethyl acetate oxidation via Mars van Krevelen mechanism [9]. Obviously small additives of titania to ceria (sample 2Ti8Ce) ensures optimal concentration of these defects and minimum segregation of pure titania phase, which provides not only high specific catalytic activity but also an increase in the selectivity in total oxidation of ethyl acetate to CO₂ as compared to the individual CeO₂.

The temperature dependencies of methanol decomposition are presented in Figure 4. Methanol decomposition provides with the formation of CO and hydrogen as the main product and CO₂, CH₄,

dimethyl ether (DME) and C₂-C₃ hydrocarbons are registered as by-products. Methanol conversion is typically observed above 500–570 K. For most of the samples, the conversion increased with the temperature and reached 70–80% at 750 K.

The appearance of well defined maximum of about 50% conversion at 675 K was observed only for TiO₂ which clearly indicates trend to deactivation. Among the tested materials, highest catalytic activity was registered for CeO₂. Note that all binary materials initiate the methanol decomposition at about 50-100 K higher temperature, but the conversion exceeds about 80% in a very narrow temperature interval (about 680 K) and no trend of deactivation is observed. To elucidate the contribution of texture parameters on the catalytic behaviour of the samples, the specific catalytic activity per unit surface area (SA) was calculated (Table 1). With the exception of 8Ti2Ce, the specific activity was very similar for all materials, which indicates the important role of both, texture and structure parameters. This was also confirmed by the changes in the selectivity during the methanol decomposition to CO and hydrogen. CO₂ was the main by-product on CeO₂ and here the highest selectivity to CO was realized. Dimethyl ether (DME) formed in

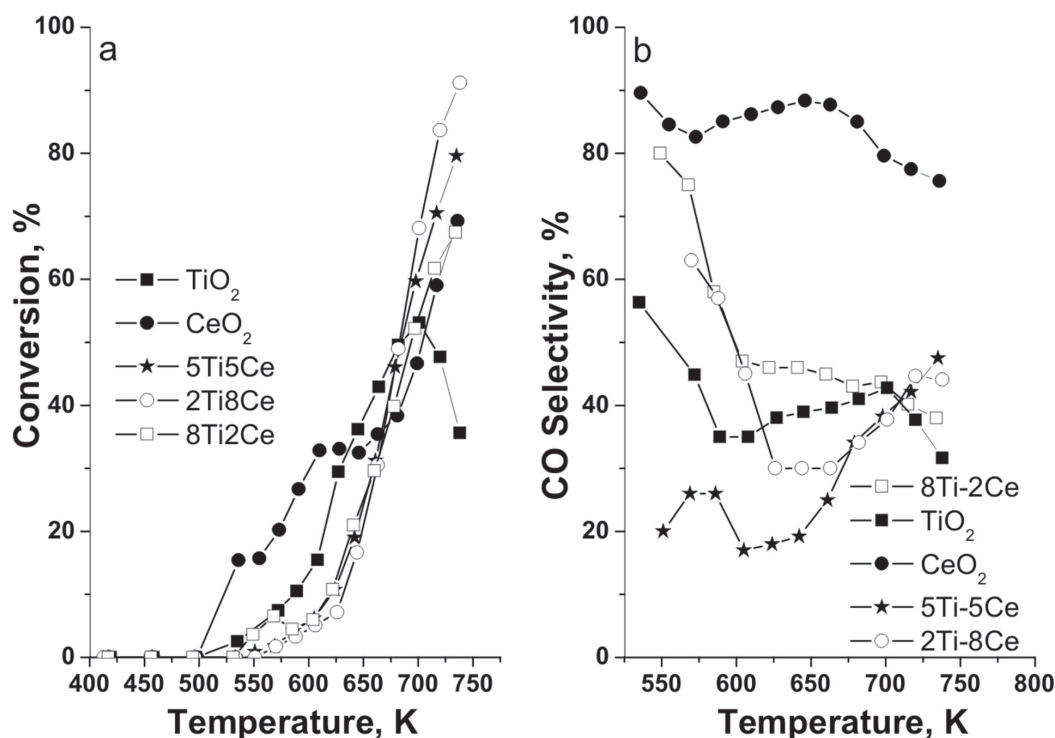
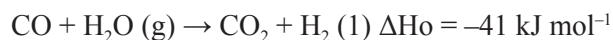


Fig. 4. Methanol conversion (a) and selectivity to CO (b) of TiCe materials.

high amount on TiO₂, indicating its high acidity. A mixture of DME and CH₄ was registered for the binary samples but their proportion was not changed in a regular way with the samples composition. The formation of CO₂ can be provided in two different reaction (1) and (2), in the presence of oxygen particles on the catalyst surface:



The strongly acidic solids, such as TiO₂, the surface methoxy groups act as methylating agents, which can react with methanol to form dimethyl ether. The α -H abstraction from the surface methoxide groups with the participation of basic oxygen ions of the solid provides the formation of aldehyde intermediates[10]. They can be bonded to the surface either *via* O and C atom through the carbonyl π^* orbital ($\eta^2(\text{C},\text{O})$ configuration) or *via* the oxygen lone pair orbital ($\eta^1(\text{O})$ configuration). Obviously, the changes in the surface electron properties of the catalyst can readily control the formation of various aldehyde species. It seems that the Lewis acidic sites, which surface density is the highest for TiO₂, facilitates the $\eta^2(\text{C},\text{O})$ configuration. The aldehyde intermediates can transform to acyl intermediate *via* hydrogen abstraction, which further decomposes to CO and H₂. Note that the $\eta^2(\text{C},\text{O})$ configuration can be stabilized on the surface in higher extent than $\eta^1(\text{O})$ configuration, which leads to desorption of the later at lower temperatures combined with decomposition to CO and H₂.

The observed specific features of the binary materials in methanol conversion clearly indicate that they are not only a result of the improved textural characteristics. The changes in the redox and acid-base properties of the samples due to the incorporation of Ti⁴⁺ in the ceria lattice probably reflects on their catalytic activity and on the selectivity to various products and this seems to be controlled in a complex way by the Ce/Ti ratio in the samples.

CONCLUSION

By using homogeneous precipitation with urea, mesoporous mono- and bi-component

Ti-Ce materials with high specific surface area and pore volume were successfully prepared. All bi-component materials demonstrate higher dispersion

and improved porous characteristics in comparison with the mono-component oxides. TPR results clearly demonstrate the existence of interaction between different metal oxide species in binary materials, which results in the presence of more readily reducible and more finely dispersed metal oxide crystallites. All bi-component oxides demonstrate specific catalytic behaviour in methanol decomposition and total oxidation of ethyl acetate, in comparison with the mono-component ones. The observed effects are in a complex relation to the improved textural characteristics of binary materials and to the specific

interaction between the individual oxides, which could be successfully controlled by the Ti/Ce ratio.

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**CeO₂ И TiO₂, ПОЛУЧЕНИ ЧРЕЗ МЕТОД НА ХОМОГЕННА ХИДРОЛИЗА
С УРЕА, КАТО КАТАЛИЗАТОРИ ЗА ОПАЗВАНЕ НА ОКОЛНАТА СРЕДА:
ЕФЕКТ НА СЪОТНОШЕНИЕ Ti/Ce**

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(Резюме)

В настоящото изследване бяха получени мезопорести Ti-Ce оксидни материали чрез хомогенно отлагане с уреа с различен състав. Образците бяха характеризирани чрез физична адсорбция на азот, XRD, UV-Vis и Раман спектроскопии, TPR, а каталитичните им свойства бяха изследвани в реакции на разлагане на метанол и окисление на етилацетат. Ефектът от фазовия състав върху текстурните, структурни и редокс свойства на образците беше дискутиран в тясна връзка с тяхната каталитична активност. Беше установено, че каталитичното поведение на образците в разлагане на метанол и окисление на етилацетат може да бъде успешно контролирано от отношението Ti/Ce.